Flux growth and liquid phase epitaxy of undoped and Mn^{6+}-doped sulfates, tungstates, and molybdates

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The Mn^{6+} ion is a promising activator ion for tunable and short-pulse laser materials because of its broadband luminescence in the spectral region 850-1600 nm and its simple $3d^1$ electronic configuration, which excludes an occurrence of undesirable exited-state absorption into higher 3d levels. However, hexavalent manganese can be stabilized only in the tetrahedral oxo-coordination and easily reduces to Mn^{5+} or Mn^{4+} at temperatures above 600°C. Recently, flux [1] and liquid-phase epitaxy (LPE) [2] growth of Mn^{6+}-doped sulfates has been reported, while except for $BaMoO_4$:Mn^{6+} [3] investigations on the mechanically more stable alkaline-earth-metal molybdates and tungstates as possible host materials for efficient Mn^{6+} incorporation have as yet not been reported.

We investigated the growth conditions of undoped and Mn^{6+}-doped MAO_4, with M = Ca, Sr, Ba and A = S, Mo, W, from the ternary NaCl-KCl-CsCl solvent at temperatures 480-600°C. The growth rates increase in the series tungstates < molybdates < sulfates and depending on the cation, in the series Ca < Sr < Ba. The dopant ion Mn^{6+} can be easily incorporated into $BaSO_4$, less well into $BaMoO_4$ and $BaWO_4$, whereas for Ca- and Sr-containing tungstates and molybdates no significant doping was found, independent on the concentration of Mn^{6+} in the liquid solution. Moreover, reduction of the Mn^{6+} ion cannot be avoided, even at the presence of oxidizing additives such as K_2CO_3 or NaOH.

LPE was employed for growing Mn^{6+}-doped layers of $BaAO_4$ compounds. Growth velocities of 3-5 µm/h in the temperature interval from 490-540°C from chloridic solution, containing 0.3-1mol% of K_2MnO_4 with respect to the solute, delivered dark-pink $BaSO_4$ and slightly green $BaMoO_4$ and $BaWO_4$ layers up to 200 µm in thickness. With respect to high Mn^{6+} doping levels, $BaSO_4$ is the most suitable host material and its further investigation under different initial concentrations of manganese is currently underway.

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